PROJECT TITLE: Near Field Emissions of MITC Following Shank

Injection and Chemigation Metam Applications

PROJECT COORDINATOR Vincent R. Hebert:

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PROJECT DURATION: September 2007 through December 2007

PROJECT SUMMARY

The focus of this work plan will evaluate putative best management pre-plant fumigation application practices to reduce off-target movement to residential communities in Franklin County, WA. A low pressure center pivot system will be identified for applying a 42% metam sodium in aqueous solution, from here referred to as metam, to a ca. 120 acre field. Close by, a field with similar acreage and soil characteristics will be concurrently treated with metam at the same rate by shank injection/soil compaction. Differences in fumigant emission of these two application demonstrations will be evaluated by monitoring near-field methyl isothiocyanate (MITC) emissions at air sampling stations located at the perimeters of the circles before, during, and 4-days after fumigant applications. In 2006, we observed a 10 fold reduction in emission by shank injection when compared to conventional chemigation during similar 2-day application periods. Moreover, a greater than four-fold reduction in surface MITC emissions was observed four days post-application on the shank injected treated field. This later observation suggests that shank injection with soil compaction can significantly reduce atmospheric loss of MITC while improving product soil retention, possibly leading to reduced rates of application and further emission reductions to surrounding communities. Unfortunately, we were not able to conduct these demonstrations at similar times. To rule out the influence of climatic factors on observed emissions, the FEQL staff with assistance from Western Farm Service will conduct near-field air monitoring in 2007 when soil-incorporated shank injection and center pivot chemigation are being performed concurrently.

APPROACH

<u>Field locations:</u> Two center pivot circles with similar soil/climatic characteristics will be identified. Each field will receive enough irrigation water to bring the field to the desired soil moisture prior to metam application. The fields will be located in a south-northerly orientation

with enough separation to minimize cross-contamination concerns. Pre-application (-1 day) air sampling will be conducted at both sites. Specific application information for each site (i.e, weather conditions during application, rate of metam application, chemigation nozzle packages used, soil depth of shanking, time for completing the application, and original observations) will be documented in a FIELD DATA BOOK (see below for data book requirements).

<u>Chemigation</u>: One field will be chemigated by center pivot (end guns operating) according to label requirements using ca. 40 gallons per acre metam with 1 inch of water. The anticipated time to complete the metam application over the circle is ca. 36 hours. Application specifics will be documented in the FIELD DATA BOOK.

<u>Soil-incorporated Shank Injection</u>: The second field will be shank injected with soil compaction at a rate of ca. 40 gallons per acre metam according to label requirements. The anticipated time to complete the metam application is ca. 2 days. Application specifics will be documented in the FIELD DATA BOOK.

<u>Air Monitoring</u>: Uniform siting procedures at the two field plots will include positioning a minimum of four mast air samplers at ca. 90° around the periphery of the circle (Figure 1). Wind speed and direction data together with soil temperature and precipitation will be gathered using a portable weather station located mid-way between the two circles and at the Ag Net weather station located at the Columbia Basin College in Pasco, WA. MITC in air will be monitored preapplication through 4 days post-application. Pre-application air sampling will be performed to determine the extent ambient MITC vapors are present near field, if at all.

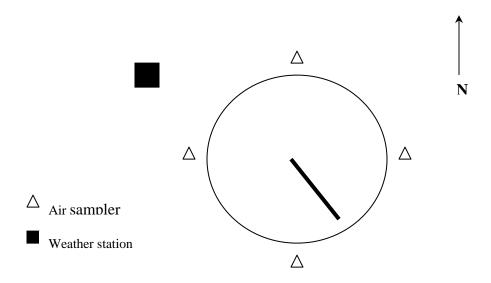


Figure 1: Center pivot air sampler locations

Sampling masts will consist of a cross-arm at approximately 1.5 -2 meter height that can hold two collocated charcoal sampling cartridges (Figure 2). Each cartridge will contain either 1-gram or 2- gram coconut charcoal (prepared by SKC West, Fullerton). The 1-gram cartridges

will be used for pre, during, zero-time, and 4 hour post-application air sampling. The 2-gram cartridges will be employed for the remainder of the post-application air sampling events. The pump flows will be set at ca. 2 liters/minute, but actual flow will be measured at the start and end of each sampling period using calibrated flow meters. Field fortifications will be performed routinely to monitor trapping efficiency over the application and post-application sampling interval period at the WSU Tri Cities campus.

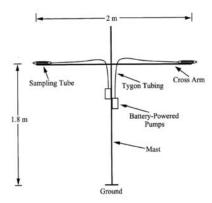


Figure 2: Sample masts with coconut charcoal cartridges

<u>Sampling Frequency and Duration</u>: The sampling masts and meteorological equipment will be operated prior to application, during application, and over a number of 4 to 12 hour sampling intervals up to 4 days post application. Samples will be taken at 4 hour air sampling intervals for pre-during application, zero and 4-hour post application samples and at 12 hour air sampling intervals for the remainder of the post application sampling events.

Proposed Number of Sampling Events

Number of samples: 2 plots x 4 stations x 2 replicates/station x 9 sample intervals (-1 day, mid application, post application time 0, 4 hour, 12 hour, 1 day, 2 day, 3 day, and 4 day) = 144 events. A minimum of 4 field fortifications with respective controls will be conducted over the application-post application interval at the WSU Tri-Cities facility.

<u>Sample Coding</u>: The samples acquired from the field will be given a sample code that will be used to track each sample as it gathered through analysis. This code will be constructed so that each site, day, collocation, time of day and trip blanks will have unique alphanumeric values that will be traceable. The coding will be as follows:

Chemigation Station Site		Co-location	
Code*	Interval Code**		Code***
Station 1 = CH1	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station 2 = CH2	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station 3 = CH3	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station 4 = CH4	-1. MID. 0. 4hr. 12hr. 1. 3. 4	R/L	Date of sampling

Shank Station Site Code*	Interval Code**	Co-location	Code***
Station 1 = SH1	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station $2 = SH2$	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station 3 = SH3	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling
Station 4 = SH4	-1, MID, 0, 4hr, 12hr, 1, 3, 4	R/L	Date of sampling

- * Station locations will be kept confidential.
- ** May be modified if sampling interval is delayed by weather conditions
- *** Date of acquired field air sample

The WSU-FEQL will attempt to conduct concurrent sampling events at both the chemigation and shank injection field locations. However, application timing and other factors such as prewatering may result in a lag in sampling between the two plot locations. Treatment blanks will accompany each shipment over ca. 7 day air sampling period and will receive a TB designation. A charcoal tube labeled **CH2-MID-L-102507** would uniquely identify the left co-located air sample taken at station 2 mid-way during chemigation on October 25th, 2007. A charcoal tube labeled **SHTB-12hr-102607** would indicate that the sample is a trip blank stored with the 12-hour post application shank samples taken on October 26th, 2007. A sample labeled **F-3-R-102907** would indicate a field fortification (F) at the WSU-TC campus taken on the 3rd day post application, October 29, 2007 from the right co-located sampling position.

Sample Handling and Quality Control: At the end of each sampling period, the sampling media will be capped with labels uniquely identifying the individual sample. The samples will be transported daily to the WSU Food and Environmental Quality Laboratory and stored at – 80° C prior to analysis. Trip blanks (i.e., no MITC) and chain of custody documentation will accompany each sample shipment. Fortified spikes will be made to the intakes of the air sampling tubes during the period of air monitoring. These tubes will be run outdoors at the WSU-Tri Cities campus for 4 hours during the pre to early post application period and for 12 hours during the longer air sampling post-application periods to verify quantitative field recovery of vapor-trapped MITC.

Laboratory Analysis: The Food and Environmental Quality Laboratory (FEQL) is a regulatory science 40 CFR Part 160 Good Laboratory Practices (GLP) facility under the direction of Dr. Hebert. Extraction and analytical methods to be used in this evaluation have been previously validated by the analysts performing the work. The Lab will employ the previously validated solvent elution method that uses an 80:20 v/v mixture of ethyl acetate/carbon disulfide for extracting MITC from charcoal air sampling tubes (FEQL, 2006). MITC in the solvent extract will be determined using gas chromatography with nitrogen-phosphorus thermionic specific detection. All steps will be taken to insure sample integrity on an analytical set-by-set basis (i.e., controls, fortifications, calibrations, and linearities). The generated data will be expressed in units of mass per volume air ($\mu g \text{ m}^{-3}$) taken over the sampling interval for assessing near-field air residues.

<u>Storage Stability</u>: An 85-day frozen storage stability study has been previously conducted by the WSU-FEQL (FEQL, 2006). It is anticipated that all sample analyses will be completed before the established 85-day storage stability period.

<u>Statistical Method</u>: Criteria for acceptance of standard curve(s) or other statistical methods shall be determined by the Project Coordinator and documented in the raw data.

<u>Field Documentation and Record Keeping</u>: All operations, data and observations appropriate to this study should be recorded directly and promptly into the FIELD DATA BOOK. General instructions for completion of the field data book can be found in this book. This data book was designed for collecting field information and serves as an authentic record of fieldwork. It has six parts or chapters containing the following information:

PART SUBJECT

- 1 Personnel Log
- 2 Communications/ Field Chronological Log and Notes
- 3 Field Trial Site Information/Placement of Air Samplers
- 4 Air Sampler Calibration/Field Testing Data Sheets
- 5 Air Sampler Shipping Information
- 6 Meteorological Records

<u>Laboratory Documentation and Record Keeping</u>: All operations, data, and observations shall be recorded in the laboratory write-ups sheets and log books, which must be signed and dated on date of entry. At a minimum, collect and maintain the following raw data:

- Analytical standard(s) receipt, use and disposition records
- Analytical standard(s) storage conditions
- Analytical standard(s) dilution calculations and preparation records
- Sample storage conditions and locations
- Calculation work sheets
- All chromatograms, including those which are not reported
- Chain of custody records
- Name of personnel conducting specific research functions
- Sample analysis laboratory write-ups sheets
- Concurrent recovery fortification records

A study file shall be developed and maintained by the FEQL Project Coordinator in conjunction with the analysis. It will contain a copy of the protocol, all pertinent raw data, documentation, records, correspondence, and the final analytical summary report. In addition, records of equipment maintenance and calibrations will be kept and periodically archived.

Analytical Summary Report: The analytical summary report shall contain, but not be limited to:

- Applicable method validation data
- Applicable storage stability data
- Residue levels for control and treated air samples with concurrent fortified recoveries
- Meteorological data
- Complete copy of the analytical Working Method
- Clearly presented example calculations or statistical evaluations

 Discussion of results (including purpose of method modifications, sample storage conditions, etc.) -summary data associated with calibration standards (dilution and use records, calibration curves, etc.)

<u>Laboratory Archives</u>: When the final analytical summary report is completed the analytical report and all original field (Field Data Book) and analytical raw data will be retained at the FEQL Testing Laboratory. All original raw data shall be secured in the FEQL Testing Laboratory archives.

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FEQL (2006). MITC Residential Community Air Assessment; South Franklin County,
Washington. Analytical Summary Report FEQL-NG-0605, 52 pp
http://feql.wsu.edu/regsci.htm

Vincent R Hebert	Date
WSU-FEQL Project Coordinator	

PROJECT TITLE: Near Field Emissions of MITC Following Shank Injection and Chemigation Metam Applications (amendment)

PROJECT COORDINATOR Vincent R. Hebert:

Changes to Protocol:

Sampling Frequency and Duration: The sampling masts and meteorological equipment will be operated prior to application, two times during application, and over a number of 4, 8 to 12 hour sampling intervals up to 8 days post application. Samples will be taken at 4 hour air sampling intervals for pre-during application and zero time. An eight hour sampling interval will be started at 4-hour post application. Twelve hour air sampling intervals will be taken for the remainder of the post application sampling events.

The WSU-FEQL will attempt to conduct concurrent sampling events at both the chemigation and shank injection field locations. However, application timing and other factors such as prewatering and weather conditions during application may result in a lag in sampling between the two plot locations. Timing of events for the chemigation field may be modified to correspond to shank field sampling timing.

Proposed Number of Sampling Events

Number of samples: 2 plots x 4 stations x 2 replicates/station x 16 sample intervals (-1 day, early application, later application, post application time 0, 4 hour, 8 hour, 1 day (two 12 hour events), 2 day (two 12-hour events), 3 day (2 12-hour events, and 4 day (2 12-hour events, and on day 8 (2 12-hour events) = 256 events. A minimum of 4 field fortifications with respective controls will be conducted over the application-post application interval at the WSU Tri-Cities facility.

<u>Sample Coding</u>: The samples acquired from the field will be given a sample code that will be used to track each sample as it gathered through analysis. This code will be constructed so that each site, day, collocation, time of day and trip blanks will have unique alphanumeric values that will be traceable. The coding will be as follows:

Chemigation Station Site		Co-location	
Code*	Interval Code**		Code***
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station $1 = CH1$	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station 2 = CH2	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station 3 = CH3	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station $4 = CH4$	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
Station 4 = CH4	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling

Shank Station Site Code	Interval Code*	Co-location	Code
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station $1 = SH1$	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station $2 = SH2$	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station 3 = SH3	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling
	-1, 1MID, 2MID, 0, 4hr, 8hr,	R/L	
	1AM, 1PM, 2AM, 2PM, 3AM,		
Station 4 = SH4	3 PM, 4 AM, 4 PM, 8 AM, 8 PM		Date of sampling

^{*} May be modified if sampling interval is delayed by weather conditions

Affect of Change on Study:

Provide continuous sampling information over the post-application 4 day period.

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